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III. *On the Composition of the Compound Sulphuret from Huel Boys, and an Account of its Crystals.* By James Smithson, Esq. F. R. S.

Read January 28, 1808.

IT is but very lately that I have seen the Philosophical Transactions for 1804, and become acquainted with the two papers on the compound sulphuret of lead, antimony, and copper contained in the first part of it, which circumstance has prevented my offering sooner a few observations on Mr. HATCHETT's experiments, which I deem essential towards this substance being rightly considered, and indeed the principles of which extend to other chemical compounds; and also giving an account of the form of this compound sulphuret, as that which has been laid before the Society is very materially inaccurate and imperfect.

We have no real knowledge of the nature of a compound substance till we are acquainted with its proximate elements, or those matters by whose direct or immediate union it is produced; for these only are its true elements. Thus, though we know that vegetable acids consist of oxygene, hydrogen, and carbon, we are not really acquainted with their composition, because these are not their proximate, that is, are not their elements, but are the elements of their elements, or the elements of these. It is evident what would be our acquaintance with sulphate of iron; for example, did we only know that a crystal of it consisted of iron, sulphur, oxygene, and

hydrogene; or of carbonate of lime, if only that it was a compound of lime, carbon or diamond, and oxygene. In fact, totally dissimilar substances may have the same ultimate elements, and even probably in precisely the same proportions; nitrate of ammonia, and hydrate of ammonia, or crystals of caustic volatile alkali,* both ultimately consist of oxygene, hydrogene, and azote.

It is not probable that the present ore is a direct quadruple combination of the three metals and sulphur, that these, in their simple states, are its immediate component parts; it is much more credible that it is a combination of the three sulphurets of these metals.

On this presumption I have made experiments to determine the respective proportions of these sulphurets in it.

I have found 10 grains of galena, or sulphuret of lead, to produce 12.5 grains of sulphate of lead. Hence the 60.1 grains of sulphate lead, which Mr. HATCHETT obtained, correspond to 48.08 grains of sulphuret of lead.

I have found 10 grains of sulphuret of antimony to afford 11.0 grains of precipitate from muriatic acid by water. Hence 31.5 grains of this precipitate are equal to 28.64 grains of sulphuret of antimony.

The want of sulphuret of copper has prevented my determining the relation between it and black oxide of copper, but this omission is, it is evident, immaterial, as the quantity of this sulphuret in the ore must be the complement of the sum of the two others.

But as the iron is a foreign adventitious substance in this ore, it follows that the foregoing quantities are the products

* FOURCROY, *Syst. des Con. Chem.* t. I. p. 88.

of only 96.65 grains of it. 100 parts of the ore are therefore composed of

Sulphuret of lead	-	49.7
Sulphuret of antimony		29.6
Sulphuret of copper	-	20.7
		<hr/>
		100.0
		<hr/>

It is impossible not to be struck with the trifling alteration which these quantities require to reduce them to very simple proportions, or to think it a very great violation of probability to suppose that experiments, effected with no errors, would have given them thus :

Sulphuret of lead	-	50.
Sulphuret of antimony	-	30.
Sulphuret of copper	-	20.

However, I doubt the existence of triple, quadruple, &c. compounds ; I believe, that *all combination is binary* ; that no substance whatever has more than two proximate or true elements ; and hence I should be inclined to consider the present compound as a combination of galena and fahlertz ; and if so, it will be accurately represented, as far as chemical analysis has yet been able to go, by the following figure :

$$\text{Compound sulphuret of lead, antimony, and copper} = \begin{cases} \frac{1}{2} \text{ galena} = \begin{cases} \frac{1}{6} \text{ sulphur} \\ \frac{1}{6} \text{ lead} \end{cases} \\ \frac{1}{2} \text{ fahlertz} = \begin{cases} \frac{3}{2} \text{ sulphuret of antimony} = \begin{cases} \frac{1}{6} \text{ sulphur.} \\ \frac{5}{6} \text{ antimony.} \end{cases} \\ \frac{2}{5} \text{ sulphuret of copper} = \begin{cases} \frac{1}{3} \text{ sulphur.} \\ \frac{2}{3} \text{ copper.} \end{cases} \end{cases} \end{cases}$$

Its ultimate elements are therefore,

Sulphur	-	20 . . . = $\frac{1}{6} \frac{2}{0}$
Lead	-	$41 \frac{2}{3}$. . . = $\frac{2}{6} \frac{5}{0}$

Antimony - $25 \dots = \frac{15}{60}$

Copper - $13\frac{1}{3} \dots = \frac{80}{60}$

and it is not a little remarkable, that here, as was the case with the calamine,* they are sexagesimal fractions of it.

When in a former paper I offered a system on the proportions of the elements of compounds, I supported it by the results of my own experiments, which might be supposed influenced, even unconsciously to myself, by a favourite hypothesis, and I made the application of it principally to a substance whose nature was not very clear. But the present case is not liable to these objections: here no fondness to the theory can be suspected of having led astray, nor did even the experiments as they came from their author's hands, bear an appearance in the least favourable to it, and yet when properly considered, they are found to accord no less remarkably with its principles.

It is evident that there must be a precise quantity in which the elements of compounds are united together in them, otherwise a matter, which was not a simple one, would be liable, in its several masses, to vary from itself, according as one or other of its ingredients chanced to predominate; but chemical experiments are unavoidably attended with too many sources of fallacy for this precise quantity to be discovered by them; it is therefore to theory that we must owe the knowledge of it. For this purpose an hypothesis must be made, and its justness tried by a strict comparison with facts. If they are found at variance, the assumed hypothesis must be relinquished with candour as erroneous, but should it, on the contrary prove, on a multitude of trials, invariably to accord with

* Phil. Trans. 1803, p. 12.

the results of observation, as nearly as our means of determination authorise us to expect, we are warranted in believing that the principle of nature is obtained, as we then have all the proofs of its being so, which men can have of the justness of their theories: a constant and perfect agreement with the phenomena, as far as can be discovered.

The great criterion in the present case is, whether on the conversion of a substance into its several compounds, and of these into one another, the simple ratios always obtain which the principles of the theory require. Amongst the multitude of instances which I could adduce, in support of such being the fact, I will, for the sake of brevity, confine myself to a few in the substances which have come under consideration above, as they will likewise give the grounds on which some of the proportions in the table have been assigned, and every chemist, by a careful repetition of the experiments, may easily determine for himself to what attention the present theory is entitled.

Lead	-	= $\frac{3}{2}$ of sulphate of lead
		= $\frac{6}{5}$ of sulphuret of lead
Sulphuret of lead	= $\frac{5}{6}$ of lead	
	= $\frac{5}{4}$ of sulphate of lead	
Sulphate of lead	= $\frac{2}{3}$ of lead	
	= $\frac{4}{5}$ of sulphuret of lead	
Antimony	-	= $\frac{4}{3}$ of powder of algorith
		= $\frac{6}{5}$ of sulphuret of antimony
Sulphuret of anti-		
mony	-	= $\frac{10}{9}$ of powder of algorith.

In the experiments by which these relations were ascertained, the portion of powder of algorith and sulphate of lead

dissolved in the precipitating and washing waters, was scrupulously collected.

The importance of a knowledge of the true quantity in which matters combine, is too evident to require to be dwelt upon; but this importance will be greatly augmented, if it should prove that this quantity is, as has been suggested, expressive of the forces with which they attract each other. It is perhaps in the form of matters that we shall find the cause of the proportions in which they unite, and a proof, *a priori*, of the system here maintained.

I have examined some of the grey ores of copper in tetrahedral crystals; but the notes of my experiments are in England. I can, however, say, that they do contain antimony, and that they do not contain iron in any material quantity. With respect to the proportions of the constituent parts, I cannot now speak with any certainty; but, I think, that at least some species of fahlertz contain a smaller portion of sulphuret of antimony, than the fahlertz does which exists as an element in the foregoing compound one.

Of the Form of this Substance.

Of the seventeen figures which have been given, as of the crystals of this compound sulphuret, in Part II. of the volume of the Transactions for 1804, great part are acknowledged to have no existence, nor are indeed any of them consistent with nature.

This substance seems to have yet offered but one form, and

which is represented in the annexed Plate under its two principal appearances ; that is, having the primitive faces, the predominant ones of the prism ; and having the secondary ones such, and which will be fully sufficient to make it known. In the first infancy of the study of crystals, it might be necessary to attend to every, the most trifling, variation of them, to trace each of their changes, step by step, to, as it were, spell the subject ; but in the state to which the science has now attained, to continue to do so would be not only superfluous, but most truly puerile.

I have a very small, but very regular, crystal of the form of Fig. 1.

By mensuration the faces *a* and *m* appear to form together an angle of about 135° , and the faces *c* and *b* an angle of about 125° .

It is said in the account above quoted, that the primitive form of this matter is a rectangular tetraedral prism, but no proofs of this have been offered ; nor have the dimensions of this prism been given, a circumstance of the first moment to the determination of true or primitive form, nor have any quantities been assigned to the decrements supposed. I will, therefore, supply these very important omissions.

That the atom of this substance is a rectangular tetraedral prism, is inferable, not from the striæ on the crystals, for striæ are by no means invariably indicative of a decrement in the direction of them ; but from the angles which the faces *a* and *c* make with the faces *m* and *b*, and these angles also prove, that the height of this prism is equal to the side of its base, that is, that it is a cube.

Hence the face *a* is produced by a decrease of one row of

atoms along the edge of the cube, and the angle it forms with the face *m* is really of 135° .

The face *c* is produced by a decrease of two rows of atoms at the corners of the cube, and the angle it forms with the face *b* is $= 125^{\circ} 15' 52''$.

The face *b* being produced like the face *a*, forms the same angle with the face *m*.

No crystal I possess, has enabled me to measure the inclinations of the faces *g*, *d*, or *f*; should the face *g*, as is presumable, result from a decrease of one row of atoms at the corners of the cube, it will form with the face *b*, an angle of $144^{\circ} 44' 8''$, and if the faces *d* and *f* are, as is also probable, produced by a decrease of two rows of atoms along the edges of the cube, the first will form an angle of $116^{\circ} 33' 54''$, and the latter one of $153^{\circ} 26' 6''$, with the face *m*.

The angles assigned here differ considerably from those given in the former account of these crystals; but the angles there given have not only appeared to me to be contradicted by observation, but, crystallographically considered, are inconsistent with each other, as the tetraedral prism of dimensions to produce an angle of 135° by a decrement along its edge, would not afford angles of 140° and 120° by decrements at its corners.

The sum of the faces of these crystals is 50.

Fig. 1.

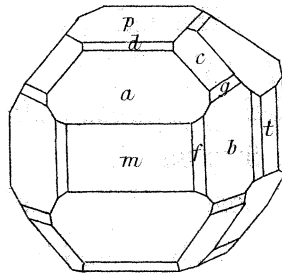
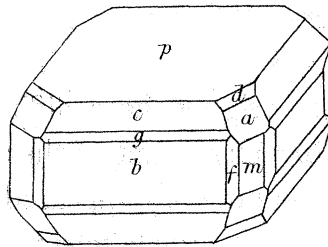


Fig. 2.



$m p$	$=$	90°		
$m t$	$=$	90°		
$a m$	$=$	135°		
$m b$	$=$	135°		
$c b$	$=$	125°	$15'$	$52''$
$g b$	$=$	144°	$44'$	$8''$
$d m$	$=$	116°	$33'$	$54''$
$f m$	$=$	153°	$26'$	$6''$